Wetting Problem For Multi-Component Fluid Mixtures

Henri Gouin [??] *and* Sergey Gavrilyuk [??]

[a] *Université d'Aix-Marseille & C.N.R.S. U.M.R. 6181*
Av. Escadrille Normandie-Niemen, Box 322, 13397 Marseille Cedex 20, France.

[b] *Université d'Aix-Marseille & C.N.R.S. U.M.R. 6595, IUSTI, Project SMASH*
5 rue E. Fermi, 13453 Marseille Cedex 13 France

hal-00260114, version 1 - 3 Mar 2008

Abstract

In this paper we propose an extension of the Cahn method [1] to binary mixtures and study the problem of wetting near a two-phase critical point without any assumption on the form of intermolecular potentials. A comparison between Cahn's method and later works by Sullivan [2,3], Evans *et al* [4,5] is made. By using an expression of the energy of interaction between solid surface and liquids proposed recently by Gouin [6], we obtain the equations of density profiles and the boundary conditions on a solid surface. In the case of a convex free-energy, a one-dimensional solution of a linear problem is proposed for the density profiles between a bulk and on a solid wall. A non-linear model of binary mixtures [7] extending Cahn's results for simple fluids is also studied. For the case of a purely attractive wall we have established a criterion of a first order transition in terms of the structure of the level set of the homogeneous part of the free energy. Additively, explicit expressions of density profiles near the wall are proposed. They allow one to consider the adsorption of mixture components by a solid wall.

Key words: Wetting problem; fluid mixtures
PACS: : 68.45.G

1 Introduction

In 1977, Cahn [1] gave simple illuminating arguments to describe the interaction between solids and liquids. His model was based on a generalized van

Email addresses: henri.gouin@univ-cezanne.fr (Henri Gouin), sergey.gavrilyuk@polytech.univ-mrs.fr (Sergey Gavrilyuk).

Preprint submitted to ***Physica A, Volume 268, Issues 3-4, Pages 291-308 (1999)***.

der Waals theory of fluids treated as attracting hard spheres [7]. It entailed assigning to the solid surface an energy that was a functional of the liquid density "at the surface". Three hypotheses are implicit in Cahn's picture for simple fluids:
(i) In order for the liquid density to be a smooth function of the distance from the solid surface, that surface is assumed to be flat on the scale of molecular sizes and the correlation length is assumed to be greater than intermolecular distances (this is the case, for example, when the temperature T is not far from the critical temperature T_c).
(ii) The forces between solid and liquid are of short range and can be described simply by adding a special energy at the solid surface.
(iii) The fluid is considered in the framework of a mean field theory. This means, in particular that the free energy of the fluid is a classical so-called "square-gradient functional".

After Cahn, the problem of adsorption and wetting was studied by a statistical method by Sullivan [2,3], Evans *et al* [4,5], respectively for gas and binary fluid mixtures. From the point of view of Sullivan and Evans *et al* one may view Cahn's approach as open to criticism for several reasons:
(a) Cahn's treatment is based on phenomenological "square-gradient" version of van der Waals theory, which in contrast to the approach initiated by van Kampen [8] does not attempt to relate directly the properties of the non-uniform fluid to the interactions occurring on a molecular level.
(b) The density adjacent to the wall vary strongly over the range of intermolecular forces, consequently the gradient expansion approximation used in deriving the square-gradient theory is no longer valid.
(c) Cahn's theory leaves unspecified a contribution due to the fluid-solid interfacial free energy.

Evans *et al* [4,5] following Sullivan's approach [2,3] for simple fluids consider the special case of a contact between a two-component mixture near "the critical end point" and a wall. They used Sullivan's grand potential to describe the solid-fluid and fluid-fluid interactions and tried to solve directly the problem of repartition of densities in a liquid (gas). Evans *et al* obtain a coupled system of integral equations for chemical potentials (cf. Eq. (6) in [4]). Then, to solve the system, it is necessary to know the interaction potentials between components and between solid wall and components: Evans *et al* assume an exponential interaction both for component-component and solid-components (as in [2,3]). Only such a hypothesis allows one to obtain two differential equations instead of the two integral equations (Eq. (10) in [4]). This assumption cannot be obviously valid for large classes of mixtures. Moreover, a special hypothesis (mixing rule) concerning interactions between components is assumed. Then, the mixing rule and exponential dependence allow one to obtain both the linear relation between potentials and boundary conditions and the problem is reduced to the problem of the contact of one-component fluid with a wall.

The phenomenological "square-gradient" model is proposed in case of an infinite non-homogeneous fluid or a fluid mixture as a small-gradient approximation by Widom [9] and Fleming *et al* [10]. The method is extended in mean-field theory for semi-infinite media in contact with a wall: as proved in [6], the fact that the densities are discontinuous at the solid wall does not disqualify the procedure used by Widom and Fleming *et al* and Cahn's treatment is valid for fluids and fluid mixtures near a critical point in contact with a wall.

In this paper, we use the expression of a surface energy. The surface is assumed to be solid and interactions between solid and fluids are sufficiently short-range. The contribution of fluids is represented by a surface free energy with a density of the form $E_S(\rho_{1S}, \rho_{2S})$, where ρ_{1S} and ρ_{2S} are the limiting densities of the fluid components at the surface. The expression of the surface energy obtained in [6] is in the form:

$$E_S \;=\; -\gamma_{11}\;\rho_{1S} - \gamma_{21}\;\rho_{2S} + \frac{1}{2}\;\left(\gamma_{12}\;\rho_{1S}^2 + \gamma_{22}\;\rho_{2S}^2 + 2\gamma_{32}\;\rho_{1S}\rho_{2S}\right). \qquad (1)$$

This expression represents first terms of a more complex expansion. It is an extension with explicit calculations of the widely known expression due to Nakanishi and Fisher [11] and examined in a review paper by de Gennes [12]. All the coefficients γ_{ij} can be calculated explicitly after the particular form of interaction potentials was chosen. For example, in the case of London forces, the values of coefficients related to the densities of the two fluids at the surface are [6]

$$\begin{aligned} \gamma_{11} \;&=\; \frac{\mu_1\pi}{12\;\delta_1^2}\;\rho_3\;, \quad \gamma_{21} \;=\; \frac{\mu_2\pi}{12\;\delta_2^2}\;\rho_3\;, \\ \gamma_{12} \;&=\; \frac{k_1\pi}{12\;\delta_1^2}\;, \quad \gamma_{22} \;=\; \frac{k_2\pi}{12\;\delta_2^2}\;, \\ \gamma_{32} \;&=\; \frac{k_3\pi}{24}\;\left(\frac{1}{\delta_1^2} + \frac{1}{\delta_2^2}\right)\;, \end{aligned} \qquad (2)$$

where ρ_3 is the density of the solid, $\mu_i,\ i \in \{1,2\}$ are the coefficients associated with intermolecular potentials of interaction between the fluids and the solid wall, $k_i,\ i \in \{1,2,3\}$ are intermolecular potentials of interaction between the molecules of fluid i and themselves or between the two fluids and $\delta_i = \frac{1}{2}(\sigma_i + \tau),\ i \in \{1,2\}$ are the minimal distances between the solid and molecules of the two species of the mixture, where $\sigma_i,\ i \in \{1,2\}$ is the diameter of molecule of fluid i and τ for the solid. Expression (1) allows us to estimate the influence of a solid wall on each component of a fluid mixture. Depending on the values of coefficients γ_{ij}, one can estimate the magnitude of the attraction or repulsion effects due to the wall.

As our approach is also based on a mean-field approximation, we assume that variations of densities near the wall take into account several molecular ranges. Hence, it is possible to present the total free energy of the system

"fluids - wall" as the sum of a bulk free energy and a surface energy which is an additional contribution arising from the non-uniformity of the fluid near the wall. By using an extended variational principle, we obtain two boundary conditions at the wall and two partial differential equations for the density profiles of the components between a solid wall and a bulk. The complete set of boundary conditions and equations for densities allow us to obtain the profiles of densities in the following physical situations. The first is the study of the linear problem associated with the equilibrium of a two-component one-phase mixture near a critical point with a solid wall. The second is the study of the non-linear problem of the contact between a two-component two-phase mixture near a critical point and a wall. We get a condition of wetting and a first order wetting transition in terms of the level set of the homogeneous part of the free energy.

To clarify the presentation some calculations are situated in Appendices. In Appendix 1, we present general calculations by using an extended variational principle applied to multi-component mixtures. In Appendix 2 we give an analytical representation of the profiles of densities connecting bulk and solid wall for a general form of the free energy of a two-component mixture near any critical point. These representations may be used to investigate the adsorption of fluid components of a mixture by a solid wall.

2 Equations of density profiles and boundary conditions: general results

The general form of the free energy per unit volume of the mixture is proposed in the form [7,10,13]

$$E = E(\rho_1, \rho_2, \nabla\rho_1, \nabla\rho_2)\,, \tag{3}$$

where ∇ notes the gradient operator in the physical space $\mathcal{D}$. The associated total free energy is

$$\mathcal{E}_{\mathcal{D}} \;=\; \int\int\int_{\mathcal{D}} E\; d\mathcal{D}.$$

The wall boundary $\mathcal{S}$ of $\mathcal{D}$ is endowed with a surface energy per unit area. The surface is solid and sharp on an atomic scale and the interactions between surface and fluids are sufficiently short range; the general form of the surface free energy per unit area used is

$$E_{\mathcal{S}} \;=\; E_{\mathcal{S}}\;(\rho_{1S}, \rho_{2S}). \tag{4}$$

Consequently, the free energy of $\mathcal{S}$ is

$$\mathcal{E}_{\mathcal{S}} \;=\; \int\int_{\mathcal{S}} E_{\mathcal{S}}\; d\mathcal{S}.$$

Then, the grand potential of the system "fluid mixture - wall" is

$$\mathcal{E} = \int\int\int_{\mathcal{D}} E \, d\mathcal{D} + \int\int_{\mathcal{S}} E_{\mathcal{S}} \, d\mathcal{S}.$$

The condition of extremum of the energy $\mathcal{E}$ based on hypotheses (3) and (4) yields (see for details Appendix 1):

- *Equations of two profiles of component densities*:

$$\nabla \left(\frac{\partial E}{\partial \rho_\alpha} - \text{div} \left(\frac{\partial E}{\partial (\nabla \rho_\alpha)} \right) \right) = 0 \quad \alpha = 1, 2 \,, \tag{5}$$

where $\dfrac{\partial E}{\partial (\nabla \rho_\alpha)}$ is the vector whose components are the partial derivatives of E with respect to the components of $\nabla \rho_\alpha$ and div is the divergence operator.

- *Two boundary conditions at the solid wall*:

$$\mathbf{n} \, \frac{\partial E}{\partial (\nabla \rho_\alpha)} + \frac{\partial E_{\mathcal{S}}}{\partial \rho_\alpha} = 0, \quad \alpha = 1, 2, \tag{6}$$

where $\mathbf{n}$ is the external unit normal vector to $\mathcal{D}$.

Equations of equilibrium (5) are the same as in [7] given for the one-dimensional case. Conditions (6) generalize those proposed in [1].

3 The dynamical system associated with one-dimensional density profiles

In the simplest case, the surface energy per unit area is given by (1) where the coefficients γ_{ij} are expressed by means of a mean-field approximation through the potentials of the intermolecular interactions (see for example (2)) and the free energy per unit volume is of the form

$$E = U(\rho_1, \rho_2) + \frac{1}{2} \left(C_1 (\nabla \rho_1)^2 + 2D \, \nabla \rho_1 \, \nabla \rho_2 \, + C_2 (\nabla \rho_2)^2 \right) , \tag{7}$$

where $U(\rho_1, \rho_2)$ is the homogeneous free energy per unit volume and C_1, C_2, D are constants such that the corresponding quadratic form is positive definite (we denote the free energy by U corresponding in [7] to $-W$).

Let us consider the case of a flat plate wall defined by equation $z = 0$ (see figure 1), where z denotes the one-dimensional coordinate orthogonal to the wall. The equations of equilibrium (6) associated with (7) are

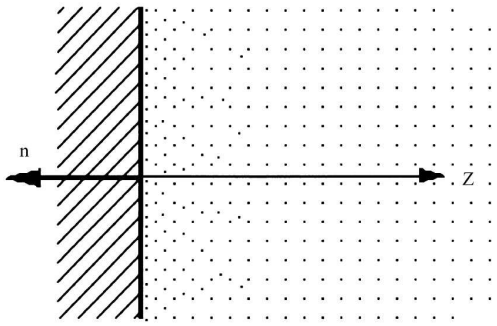

Fig. 1. *One-dimensional contact of a fluid with a wall.*

$$\begin{cases} C_1 \dfrac{d^2\rho_1}{dz^2} + D \dfrac{d^2\rho_2}{dz^2} = \dfrac{\partial U}{\partial \rho_1}(\rho_1, \rho_2) + e_1 \\ D \dfrac{d^2\rho_1}{dz^2} + C_2 \dfrac{d^2\rho_2}{dz^2} = \dfrac{\partial U}{\partial \rho_2}(\rho_1, \rho_2) + e_2 \end{cases} \tag{8}$$

where e_1 and e_2 are two constants of integration.

These equations are complemented by the boundary conditions (6) at $z = 0$. By using expression (1) of the surface energy, we get

$$\begin{cases} C_1 \dfrac{d\rho_1}{dz} + D \dfrac{d\rho_2}{dz} = -\gamma_{11} + \gamma_{12}\rho_1 + \gamma_{32}\rho_2 \\ D \dfrac{d\rho_1}{dz} + C_2 \dfrac{d\rho_2}{dz} = -\gamma_{21} + \gamma_{32}\rho_1 + \gamma_{22}\rho_2 \end{cases} \tag{9}$$

We have to add the condition in the bulk (at $z = +\infty$):

$$\rho_1 = \rho_{1\infty}, \;\; \rho_2 = \rho_{2\infty}\,. \tag{10}$$

4 Linear wetting problem

We consider the case of a one-phase mixture (liquid or gas) in contact with a solid wall. The densities of the two-components and the temperature are close to critical conditions. Moreover, we assume that density variations are small enough with respect to bulk densities, i.e.

$$\frac{\rho_i - \rho_{i\infty}}{\rho_{i\infty}} << 1, \quad i = 1, 2$$

such that we can consider a linearized problem associated with equations (8). Let us denote

$$\mathbf{r} = \begin{pmatrix} \rho_1 - \rho_{1\infty} \\ \rho_2 - \rho_{2\infty} \end{pmatrix}, \quad \mathbf{q} = -\begin{pmatrix} \gamma_{11} \\ \gamma_{21} \end{pmatrix} + \Gamma \begin{pmatrix} \rho_{1\infty} \\ \rho_{2\infty} \end{pmatrix} \equiv -\boldsymbol{\gamma} + \Gamma \boldsymbol{\rho}_\infty,$$

$$\Gamma = \begin{pmatrix} \gamma_{12} & \gamma_{32} \\ \gamma_{32} & \gamma_{22} \end{pmatrix}, \quad A = \begin{pmatrix} C_1 & D \\ D & C_2 \end{pmatrix}, \quad B = \begin{pmatrix} \frac{\partial^2 U}{\partial \rho_1^2} & \frac{\partial^2 U}{\partial \rho_1 \partial \rho_2} \\ \frac{\partial^2 U}{\partial \rho_1 \partial \rho_2} & \frac{\partial^2 U}{\partial \rho_2^2} \end{pmatrix}. \tag{11}$$

The matrix B is calculated in the bulk $(\rho_{1\infty}, \rho_{2\infty})$. Taking into account the definitions (11), we get the linearized problem associated with equations (8)-(10) in the form:

$$A\frac{d^2\mathbf{r}}{dz^2} = B\mathbf{r} \tag{12}$$

$$A\frac{d\mathbf{r}}{dz} = \mathbf{q} + \Gamma\mathbf{r} \quad \text{at} \quad z = 0 \tag{13}$$

$$\mathbf{r} = 0 \quad \text{at} \quad z = +\infty. \tag{14}$$

The stability of the thermodynamic state of the bulk requires that the symmetric matrix B is also positive definite.

Let χ_i^2, $\mathbf{h}_i$ be the eigenvalues and the eigenvectors of the equation

$$\left(B - \chi_i^2 A\right)\mathbf{h}_i = \mathbf{0}.$$

Since B and A are symmetric and positive definite, χ_i^2 are positive. We can always suppose that [1]

$$\mathbf{h}_i A \mathbf{h}_j = 0, \quad i \neq j\,.$$

The solution of (12) satisfying the condition (14) is in the form

$$\mathbf{r} = \sum_{i=1}^{2} b_i \mathbf{h}_i \exp(-\chi_i z) \quad \text{where} \quad \chi_i > 0\,. \tag{15}$$

Substituting expression (15) into condition (13), we get a linear system of algebraic equations for the unknown coefficients b_i

$$\sum_{i=1}^{2} b_i(\Gamma + \chi_i A)\mathbf{h}_i = -\mathbf{q}$$

which defines a unique solution b_i if $det(\mathbf{h}_i\Gamma\mathbf{h}_j + \chi_i\mathbf{h}_i A\mathbf{h}_j) \neq 0$. In particular, if Γ is negligible (we assume that the wall is purely attractive), we get $\mathbf{q} = -\boldsymbol{\gamma}$

[1] $\overline{\mathbf{V}N\mathbf{W}} \equiv \mathbf{V} \otimes (N\mathbf{W})$ denotes the bilinear form of vectors $\mathbf{V}$ and $\mathbf{W}$ with respect to matrix N; the bilinear form is symmetric when matrix N is symmetric.

(see (11)) and

$$b_i = \frac{\boldsymbol{\gamma}\ \mathbf{h}_i}{\chi_i(\mathbf{h}_i A \mathbf{h}_i)}\,.$$

In such a case, the solutions satisfy conditions (13) and the density profiles fulfil the solution of linearized problem. Equations (15) yield different forms of density profiles. Depending on wall conditions, we may obtain both monotonic and non-monotonic profiles. This is similar to results of [7] in the non-linear case without a solid wall. In figure 2, we represent the different density profiles for each component of the mixture. We note that only one extremum point may appear for each density profile. This result is different from the results of Evans *et al* where density profiles are essentially monotonic.

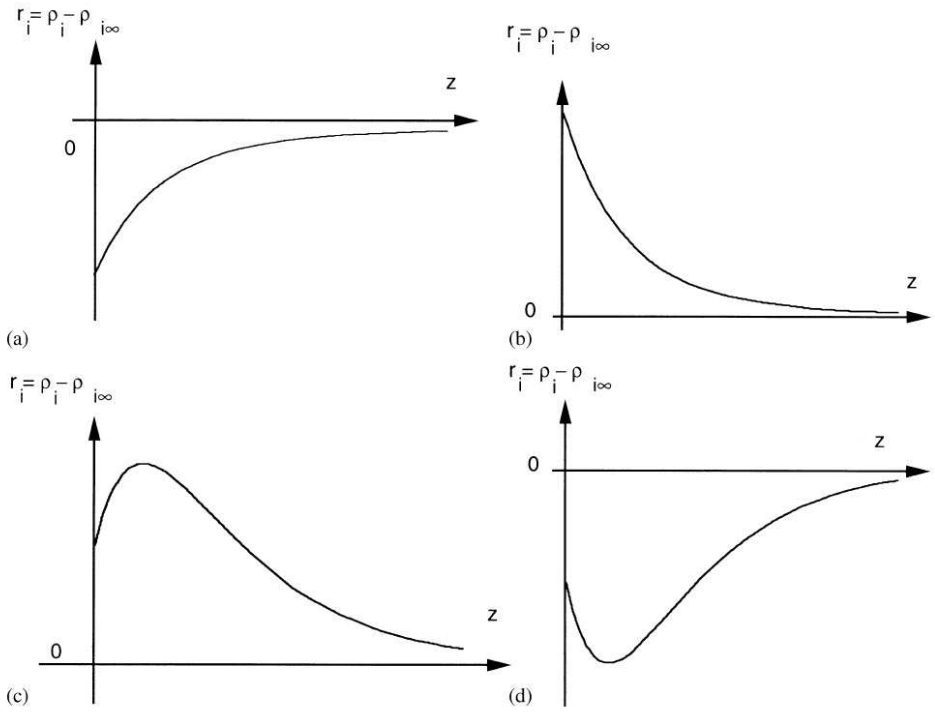

Fig. 2. *In (a) and (b) the profiles of densities for a component are monotonic. In (c) and (d) the profiles admit an extremum of density for a component. The extremum is not on the wall but at some distance into the bulk measured on a molecular scale.*

5 Wetting problem near a critical point for a two-component mixture

5.1 The dynamical system

In a two-phase region near a critical point at a given temperature T, the expression of the free energy per unit volume U associated with a phase equilibrium is of the form [7]

$$U = a_0^2\Big((b_0^2x^2 + y)^2 + (y + t)^2\Big). \tag{16}$$

The parameter t is an independently varied field characterizing the "distance" from the critical point (ρ_{1c}, ρ_{2c}), a_0 and b_0 are functions of the temperature. The variables x and y are defined through the transformation

$$\mathbf{r} = \Delta\mathbf{R}, \quad \mathbf{R} = \begin{pmatrix} x \\ y \end{pmatrix}, \quad \Delta = \begin{pmatrix} a & b \\ c & d \end{pmatrix}, \quad \mathbf{r} = \boldsymbol{\rho} - \boldsymbol{\rho}_c,$$

$$\boldsymbol{\rho} = \begin{pmatrix} \rho_1 \\ \rho_2 \end{pmatrix}, \quad \boldsymbol{\rho}_c = \begin{pmatrix} \rho_{1c} \\ \rho_{2c} \end{pmatrix}. \tag{17}$$

The scalars a, b, c, d associated with the physical properties of the mixture near the critical point depend on the temperature T. The constants of integration $e_1 = 0$ and $e_2 = t$ are already incorporated in U. With Eq. (17), the system (8) can be rewritten in the form

$$\Delta^\star A\Delta\frac{d^2\mathbf{R}}{dz^2} = \nabla_{\mathbf{R}}U, \tag{18}$$

where $\Delta^\star$ denotes the transpose matrix and $\nabla_{\mathbf{R}}U$ means the gradient with respect to $\mathbf{R}$.
Following Rowlinson and Widom [7] we denote by

$$M = \Delta^\star A\Delta = \begin{pmatrix} m_{xx} & m_{xy} \\ m_{xy} & m_{yy} \end{pmatrix}. \tag{19}$$

Obviously, if A is positive definite, M is also positive definite, i.e. $m_{xx} > 0$, $m_{xx}m_{yy} - m_{xy}^2 > 0$. The boundary conditions (9) at the wall are

$$M\frac{d\mathbf{R}}{dz} = \mathbf{g} + G\ \mathbf{R}, \quad \text{where} \quad \mathbf{g} = \Delta^\star(-\boldsymbol{\gamma} + \Gamma\boldsymbol{\rho}_c) \quad \text{and} \quad G = \Delta^\star\Gamma\Delta\,. \tag{20}$$

In the following, we choose in Eq. (16) $a_0 = 1/\sqrt{2}$ and $b_0 = 1$ (to do this, we have only to change the values of coefficients of the matrix Δ defined by (17)).

Hence, $\quad U = \frac{1}{2}\Big((x^2+y)^2 + (y+t)^2\Big)$.

The system (18)-(19) yields

$$\begin{cases} m_{xx}\dfrac{d^2x}{dz^2} + m_{xy}\dfrac{d^2y}{dz^2} = 2x(x^2+y) \\ m_{xy}\dfrac{d^2x}{dz^2} + m_{yy}\dfrac{d^2y}{dz^2} = x^2 + 2y + t \end{cases} \tag{21}$$

System (21) admits the first integral

$$\frac{1}{2}\ m_{xx}(\frac{dx}{dz})^2 + \ m_{xy}(\frac{dx}{dz})(\frac{dy}{dz}) + \frac{1}{2}\ m_{yy}(\frac{dy}{dz})^2 - U(x,y) = 0. \tag{22}$$

This integral is similar to the integral of energy for mechanical problems.

Substitution of boundary conditions (20) into the relation (22) yields necessary conditions for x, y at the solid wall. For simplicity, we consider only the case of an attractive wall (G is then negligeable). Conditions (20) yield

$$M\frac{d\mathbf{R}}{dz} = \mathbf{g}. \tag{23}$$

In fact, it is natural to expect that the results we obtain in the case of an attractive wall are closely similar to the results associated with the most general case. Relations (22) and (23) yield

$$U(x,y) = k^2,$$

where $k^2 = \mathbf{g}M^{-1}\mathbf{g}$. Then, discussion of the wetting of a fluid mixture with a solid wall arises naturally from the drawing of the level curves of U(x,y) as a function of the parameter t.

5.2 Connection between the dynamical system and Young's conditions

For a solid wall in contact with phases α and β, the contact angle θ is defined with the help of surface free energies σ along the solid surface (Young's conditions)

$$\sigma_{\alpha\beta}\ cos\theta = \sigma_{\alpha S}\ -\ \sigma_{\beta S}\,. \tag{24}$$

where the different subscripts designate phases adjoining the surface or interface. No value of θ satisfies Eq. (24) unless

$$\sigma_{\alpha\beta} > \mid \sigma_{\alpha S}\ -\ \sigma_{\beta S}\ \mid. \tag{25}$$

If the inequality (25) is not satisfied, one of the fluid phases completely wets the solid and there is no contact between solid and other fluid phase. In fact,

the forbidden surface is replaced by a layer of the wetting phase and the surface free energy becomes the sum of two surfaces' free energies of the layer

$$\sigma_{\alpha S} = \sigma_{\alpha\beta} \ + \ \sigma_{\beta S}. \tag{26}$$

Condition (26) corresponds to the perfect wetting with the solid. The surface energies can be calculated by the formulas

$$\sigma_{\alpha\beta} = \int_{-\infty}^{+\infty} (K+U)dz, \quad \sigma_{\alpha S} = \int_{0}^{+\infty} (K+U)dz, \quad \sigma_{\beta S} = \int_{0}^{+\infty} (K+U)dz,$$

where $K = \frac{1}{2}\, m_{xx}(\frac{dx}{dz})^2 + \ m_{xy}(\frac{dx}{dz})(\frac{dy}{dz}) + \frac{1}{2}\, m_{yy}(\frac{dy}{dz})^2$ and integrals are taken on different paths connecting phase α and phase β or a phase and the wall [7].

Let us note $(ds)^2 = \frac{1}{2}\, m_{xx}(dx)^2 + \ m_{xy}dxdy + \frac{1}{2}\, m_{yy}(dy)^2$.

From the first integral (22), we get

$$\sigma_{\alpha\beta} = \int_{(x_\alpha, y_\alpha)}^{(x_\beta, y_\beta)} (2U(x,y))^{\frac{1}{2}} ds, \qquad \sigma_{\alpha S} = \int_{(x_{M_\alpha}, y_{M_\alpha})}^{(x_\alpha, y_\alpha)} (2U(x,y))^{\frac{1}{2}} ds,$$

$$\sigma_{\beta S} = \int_{(x_{M_\beta}, y_{M_\beta})}^{(x_\beta, y_\beta)} (2U(x,y))^{\frac{1}{2}} ds\,. \tag{27}$$

The integrals (27) are calculated on the paths associated with system (21) and the boundary conditions on the wall

$$x = x_{M_\alpha}, \quad y = y_{M_\alpha} \quad \text{or} \quad x = x_{M_\beta}, \quad y = y_{M_\beta},$$

and in the bulks

$$x = x_\alpha, \quad y = y_\alpha \quad \text{or} \quad x = x_\beta, \quad y = y_\beta.$$

5.3 Discussion of the wetting

For a solid wall the value of k^2 is given. Hence, the discussion depends on the relative value of parameter t.

(a) $t > 0$ and large enough.

In this case we are far enough from the critical conditions. In figure 3a the phases are in points $A(x_\alpha, y_\alpha)$ and $B(x_\beta, y_\beta)$. One obtains easily that $x_\alpha =$

$-\sqrt{t},\ y_\alpha = -t,\ x_\beta = \sqrt{t},\ y_\beta = -t$. The points M_α and M_β belong to two different connected components of the level set $U = k^2$. In the vicinity of A (or B), the energy U is a convex function of x, y and as in Section 4, it is possible to find the profiles of densities connecting A and M_α or B and M_β, respectively. The integrals (27) are positive and $\sigma_{\alpha,\beta}$ is large with respect to $\sigma_{\alpha,S}$ and $\sigma_{\beta,S}$. Then the relations

$$\sigma_{\alpha,S} \leq \sigma_{\alpha,\beta} + \sigma_{\beta,S} \quad \text{and} \quad \sigma_{\beta,S} \leq \sigma_{\alpha,\beta} + \sigma_{\alpha,S} \tag{28}$$

hold and we are in the case of partial wetting with $\theta \neq 0$.

(b) $t > 0$ and small enough.

This case corresponds to phases close enough to the critical point (see figure 3b). The level set $U = k^2$ consists only of one connected component containing the points M_α and M_β. The phases are at the points $A(x_\alpha, y_\alpha)$ and $B(x_\beta, y_\beta)$. They are very close with respect to the distance to the level curve. The superficial tension $\sigma_{\alpha,\beta}$ is small with respect to the free energies $\sigma_{\alpha,S}$ and $\sigma_{\beta,S}$. The values of $\sigma_{\alpha,S}$ and $\sigma_{\beta,S}$ are in general different and one of the two relations (28) is not satisfied. We are in the case where one of the two phases wets completely the solid wall. No contact appears between the other phase and the solid. For exemple, if relation (26) is satisfied, the phase β wets completely the wall.

(c) $t < 0$

The mixture has only one phase at the point $A(0, -t/2)$, which is the only singular point of the system (21). The energy U attains a minimum at the point A (we note that for $t > 0$ this point corresponds to a saddle point, which is not associated with a bulk phase). The free energy U of the mixture is convex at the vicinity of A (figures 3c and 3d). If t is small enough, the linear solution for the profiles of densities obtained in Section 4 can be used. When t is large enough, the solution for the profiles of densities can be calculated analogously as in the Appendix 2.

5.4 Some remarks on the profiles of densities

The system (21) yields

$$M \ \frac{d^2\mathbf{R}}{dz^2} \ = \ \begin{pmatrix} 2x(x^2+y) \\ x^2 + 2y + t \end{pmatrix} \tag{29}$$

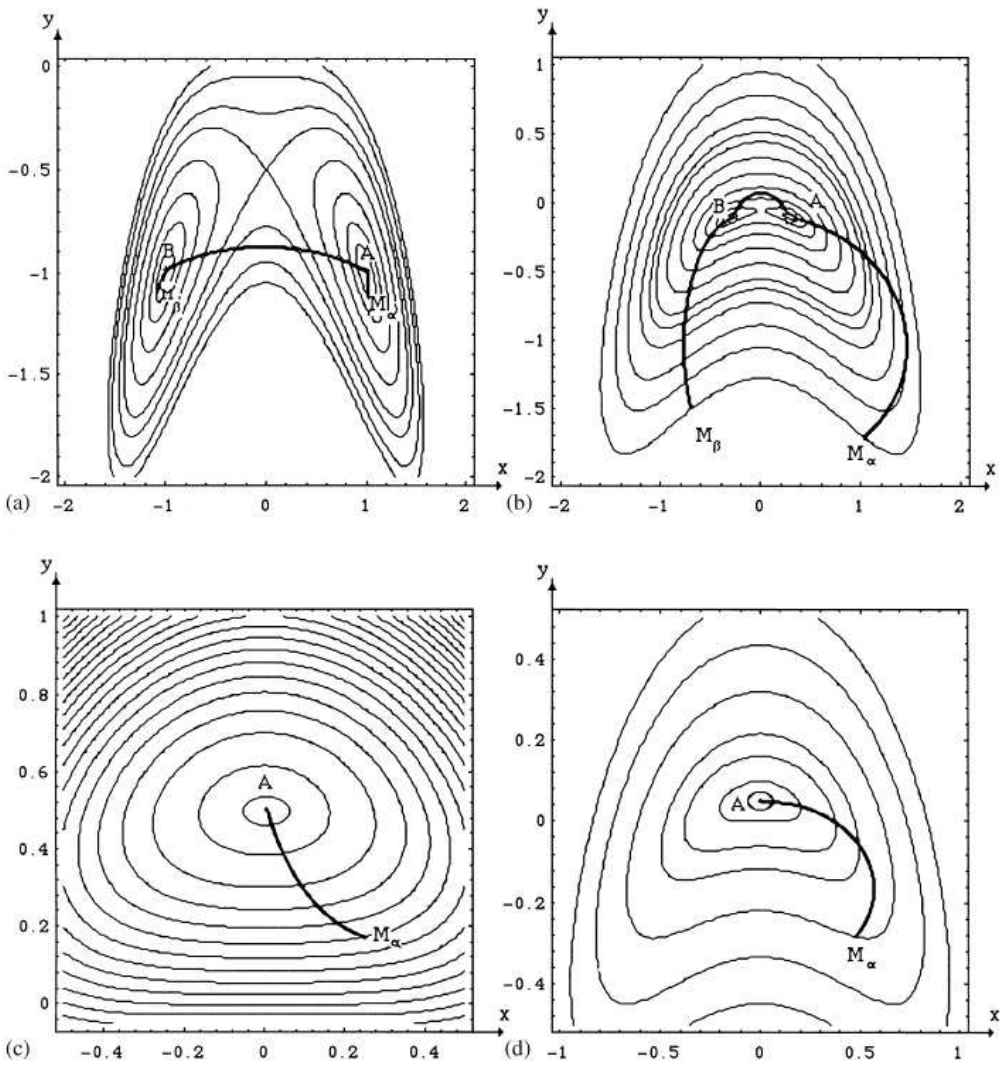

Fig. 3. *Drawing of level curves for the free energy U for different values of t. Points A (and B) correspond to the bulks. The bold curves are paths connecting a phase and the solid wall or two phases. The interfacial tension is calculated along these paths. (a) is the case of partial wetting with a non-zero Young angle. The other figures are associated with different cases of total wetting of one phase: in (b) with two phases and in (c) and (d) with one phase.*

and admits the first integral (22):

$$\frac{d\mathbf{R}}{dz}\, M\, \frac{d\mathbf{R}}{dz} \;-\; (x^2+y)^2 - (y+t)^2 = 0. \tag{30}$$

When the densities x, y are far from critical conditions, t is negligeable with respect to x and y and (30) reads

$$\frac{d\mathbf{R}}{dz}\, M\, \frac{d\mathbf{R}}{dz} \;-\; (x^2+y)^2 - y^2 = 0. \tag{31}$$

Let us denote $V(z) = \mathbf{R}M\mathbf{R}$. Then, by using (29) and (31), we get $\dfrac{d^2V}{dz^2} = 3x^4 + 5x^2y + 3y^2$. The right-hand side is a positive definite quadratic form, which implies that

$$\frac{d^2V}{dz^2} > 0\,.$$

Hence,

$$V(z) \geq V(0) + V'(0)z\,.$$

If $\left.\dfrac{dV}{dz}\right|_{z=0} > 0$, it follows from here that $V \to \infty$ as $z \to \infty$. The level curves of V are represented in figure 4a. Hence, x or y must be an increasing function of z near the solid wall. For example, let x be an increasing function of z when z is small enough. Due to the fact that $x \to \pm\sqrt{t}$ as $z \to +\infty$ and t is small with respect to $x(0)$, the representation of x as a function of z has the form shown in figure 4b. Hence, the function $x(z)$ is non-monotonic. In this case we may have also non-monotonic profiles of densities unlike in the treatment of Evans et al. Then, construction of an analytical solution may be done according to the algorithm proposed in Appendix 2.

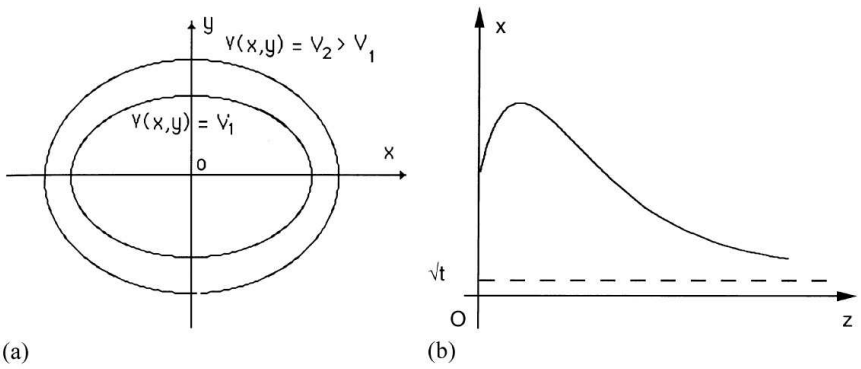

Fig. 4. *(a) represents level sets of V. Since x or y must be an increasing function of z near the wall, due to the limit conditions at infinity, x or y is a non-monotonic function of z. (b) is a representation of such a function.*

6 Conclusion

Near critical conditions, by using a variational approach, we have obtained for an isothermal binary mixture in contact with a solid wall equations of equilibrium and boundary conditions which generalize those obtained by Cahn. With limit conditions in the bulk, they form a closed boundary value problem. When the free energy of the mixture is a quadratic form with respect to the densities of components and their gradients, we get explicit profiles of the densities in the one-dimensional case.

In the case of a purely attractive wall we have also established a criterion of a first order transition, when a contact angle against a solid wall becomes zero. This criterion is formulated in terms of the level set of the function $U(x,y)$: $U(x,y) = k^2$, where k^2 depends on the boundary conditions. If the level set is a connected set, two multi-component layers exist: one layer with ordinary adsorption and the second one in contact with the wetting layer. If the level set is disconnected we have partial wetting. We have also shown that the profiles of density are typically non-monotonic. This is in agreement with Rowlinson and Widom [7] where infinite two-phase two-component mixtures where considered.

Acknowledgements

We have greatly benefited from comments and advises of Professor Benjamin Widom.

Appendix 1. Calculus of variations for fluid mixtures

We study a two-fluid equilibrium, but the method can be extended to any number of components. The position of a two-fluid mixture is associated with two applications

$$\mathbf{x} \;=\; \boldsymbol{\phi}_\alpha\,(\mathbf{X}_\alpha),\;\; \alpha = 1,2,$$

where $\mathbf{X}_\alpha$ denote the Lagrangian coordinates belonging to a reference space $\mathcal{D}_\alpha$ associated with the αth component and $\mathbf{x}$ denotes the Eulerian coordinates in the physical space $\mathcal{D}$ [13]. The virtual motions of particles are deduced from the relation

$$\mathbf{x} = \boldsymbol{\Phi}_\alpha(\mathbf{X}_\alpha, \varepsilon_\alpha),\;\; \boldsymbol{\Phi}_\alpha(\mathbf{X}_\alpha, 0) \;= \boldsymbol{\phi}_\alpha(\mathbf{X}_\alpha)\,.$$

Here $\varepsilon_\alpha,\;\alpha = 1,2$ are small parameters defined in a neighbourhood of zero. Virtual displacement $\boldsymbol{\zeta}_\alpha$ are defined by [13,14]

$$\boldsymbol{\zeta}_\alpha \;= \frac{\partial \boldsymbol{\Phi}_\alpha}{\partial \varepsilon_\alpha}(\mathbf{X}_\alpha, \varepsilon_\alpha)_{\big|_{\varepsilon_\alpha = 0}}, \quad \alpha = 1,2\,. \tag{A1}$$

At the solid boundary, the virtual displacement $\boldsymbol{\zeta}_\alpha$ is subject to the conditions

$$\mathbf{n}\,\boldsymbol{\zeta}_\alpha = 0,\;\; \alpha = 1,2\,, \tag{A2}$$

where $\mathbf{n}$ is the unit normal vector to the boundary.

Eulerian variations of densities are defined by

$$\delta_\alpha \rho_\alpha = \frac{d}{d\varepsilon_\alpha}\rho_\alpha(\mathbf{x}, \varepsilon_\alpha)_{\big|_{\varepsilon_\alpha = 0}} \quad \text{and} \quad \delta_\alpha \rho_\beta = 0, \quad \beta \neq \alpha, \quad \alpha, \beta = 1,2\,. \tag{A3}$$

The variations (A3) are related to the virtual displacements (A1) by the formulae [14,15]

$$\delta_\alpha \rho_\alpha = -\mathrm{div}(\rho_\alpha\, \boldsymbol{\zeta}_\alpha)\ , \quad \alpha = 1, 2. \tag{A4}$$

The variations of the volume free energy are

$$\delta_\alpha \mathcal{E}_\mathcal{D} \ = \ \int\int\int_\mathcal{D} \delta_\alpha E d\mathcal{D},$$

where

$$\delta_\alpha E \ = \ \frac{\partial E}{\partial \rho_\alpha}\delta_\alpha \rho_\alpha \ + \ \mathbf{f}_\alpha\ \delta_\alpha \nabla \rho_\alpha \quad \text{with} \quad \mathbf{f}_\alpha \ = \frac{\partial E}{\partial(\nabla \rho_\alpha)}\,.$$

Since

$$\delta_\alpha \nabla \rho_\alpha \ = \ \nabla(\delta_\alpha \rho_\alpha)$$

we get

$$\delta_\alpha \mathcal{E}_\mathcal{D} \ = \ \int\int\int_\mathcal{D} \left(\frac{\delta E}{\delta \rho_\alpha}\, \delta_\alpha \rho_\alpha + \ \mathrm{div}\ (\mathbf{f}_\alpha\, \delta_\alpha \rho_\alpha) \right) d\mathcal{D}, \tag{A5}$$

where the variational derivative $\dfrac{\delta E}{\delta \rho_\alpha}$ is defined by

$$\frac{\delta E}{\delta \rho_\alpha} \ \equiv \ \frac{\partial E}{\partial \rho_\alpha} \ - \ \mathrm{div}\ \mathbf{f}_\alpha.$$

From relations (A2), (A4) and (A5) we obtain

$$\delta_\alpha \mathcal{E}_\mathcal{D} \ = \ \int\int\int_\mathcal{D} \left(\rho_\alpha \nabla \left(\frac{\delta E}{\delta \rho_\alpha} \right) \boldsymbol{\zeta}_\alpha - \ \mathrm{div}\ \left(\rho_\alpha \frac{\delta E}{\delta \rho_\alpha}\, \boldsymbol{\zeta}_\alpha + \mathbf{f}_\alpha\ \mathrm{div}\ (\rho_\alpha \boldsymbol{\zeta}_\alpha) \right) \right)\ d\mathcal{D}$$

$$= \ \int\int\int_\mathcal{D} \ \rho_\alpha \nabla \left(\frac{\delta E}{\delta \rho_\alpha} \right) \boldsymbol{\zeta}_\alpha \ d\mathcal{D} - \int\int_\mathcal{S} \mathbf{n}\ \mathbf{f}_\alpha\ \mathrm{div}\ (\rho_\alpha \boldsymbol{\zeta}_\alpha) d\mathcal{S}\,.$$

The variations of the surface free energy are

$$\delta_\alpha \mathcal{E}_\mathcal{S} = \ \int\int_\mathcal{S} \frac{\partial E_\mathcal{S}}{\partial \rho_\alpha}\, \delta_\alpha \rho_\alpha d\mathcal{S} = \ -\int\int_\mathcal{S} \frac{\partial E_\mathcal{S}}{\partial \rho_\alpha}\, \mathrm{div}(\rho_\alpha \boldsymbol{\zeta}_\alpha) d\mathcal{S}\,.$$

The grand potential of the system is $\mathcal{E} = \mathcal{E}_\mathcal{D} + \mathcal{E}_\mathcal{S}$ and its αth variation is given by the formula

$$\delta_\alpha \mathcal{E} = \ \int\int\int_\mathcal{D} \ \rho_\alpha \nabla \left(\frac{\delta E}{\delta \rho_\alpha} \right) \boldsymbol{\zeta}_\alpha \ d\mathcal{D} \ - \int\int_\mathcal{S} \left(\mathbf{n}\ \mathbf{f}_\alpha + \frac{\partial E_\mathcal{S}}{\partial \rho_\alpha} \right)\ \mathrm{div}\ (\rho_\alpha \boldsymbol{\zeta}_\alpha) d\mathcal{S}\,.$$

Denoting $c_\alpha = \mathbf{n}\, \mathbf{f}_\alpha + \dfrac{\partial E_\mathcal{S}}{\partial \rho_\alpha}$, we obtain

$$\int\int_\mathcal{S} c_\alpha \mathrm{div}(\rho_\alpha \boldsymbol{\zeta}_\alpha) d\mathcal{S} = \int\int_\mathcal{S} \left(c_\alpha\ \mathrm{div}_\mathcal{S}(\rho_\alpha \boldsymbol{\zeta}_\alpha) + c_\alpha \left(\mathbf{n} \frac{\partial(\rho_\alpha \boldsymbol{\zeta}_\alpha)}{\partial \mathbf{x}} \mathbf{n} \right) \right) d\mathcal{S}\,,$$